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Title:	Los Alamos National Laboratory Method for 235U-231Pa Chronometry Measurements
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LA-UR Number

Los Alamos National Laboratory Method for ^{235}U-^{231}Pa Chronometry Measurements

CIAE/USDOE NSDD Meeting

November 6, 2018

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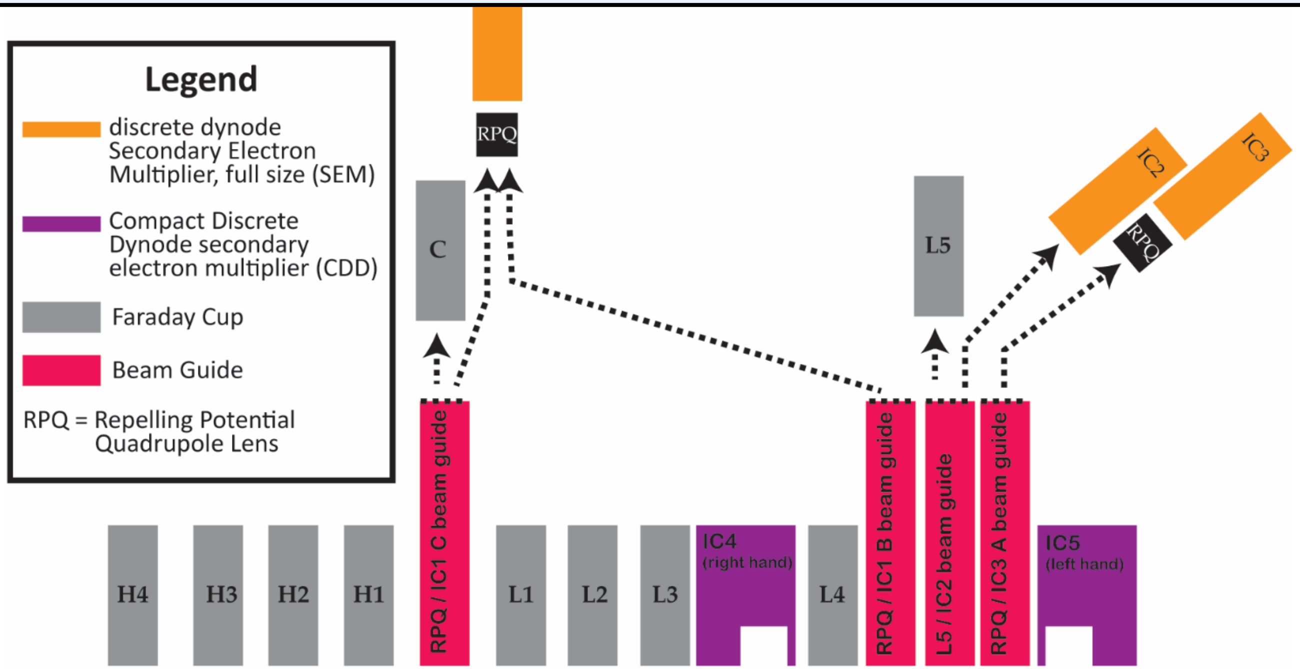
^{235}U-^{231}Pa Chronometry Sample Analysis

- Thermo Scientific Neptune Plus used to analyze chronometry samples
  - Multi-collector ICP-MS with desolvating sample introduction system
- Separate cup configurations for measuring PaT (traced Pa) UxI (untraced U), and UxT (traced U) fractions
- Strategies for correcting instrumental effects
  - Mass bias, gain, abundance sensitivity



Traced Pa: Cup Configuration

Traced Pa Sequence

U-010
Wash 1
Wash 2
Acid Blank
U-005A
Wash 1
Wash 2
Acid Blank
PaT Sample 1
Wash 1
Wash 2
Acid Blank
PaT Sample 2
Wash 1
Wash 2
Acid Blank
U-010
Wash 1
Wash 2
Acid Blank
U-005A
⋮

Traced Pa Neptune Plus Cup Configuration					
	IC5	IC3	IC2/ L5	IC1 B	L4
PaT Samples		231Pa	232Th	233Pa	235U
U Standards	233U	234U	235U	236U	238U

Ion Counter

Faraday

Pa Sample Fractions

- ^{231}Pa and ^{233}Pa on full-size SEMs (~10,000-120,000 cps)
- ^{235}U (Faraday) to confirm purification of Pa fraction
- ^{232}Th (SEM) to monitor potential ^{232}Th+H interference on ^{233}Pa

U Bracketing Standards

- No certified Pa standards
- ^{235}U and ^{238}U on Faradays, ^{234}U and ^{236}U on full-size SEMs

Traced Pa: Instrument Bias

Traced Pa Sequence

- U-010
- Wash 1
- Wash 2
- Acid Blank
- U-005A
- Wash 1
- Wash 2
- Acid Blank
- PaT Sample 1
- Wash 1
- Wash 2
- Acid Blank
- PaT Sample 2
- Wash 1
- Wash 2
- Acid Blank
- U-010
- Wash 1
- Wash 2
- Acid Blank
- U-005A
- ⋮

U010
Mass Bias and Gain Corrections

U005A
QC Standard

Traced Pa Neptune Plus Cup Configuration

	IC5	IC3	IC2/ L5	IC1 B	L4
PaT Samples		231Pa	232Th	233Pa	235U
U Standards	233U	234U	235U	236U	238U

Ion Counter

Faraday

Exponential Mass Bias Correction

$$\beta = \frac{ln\left(\frac{R^{235/238}_{True}}{R^{235/238}_{Meas}}\right)}{ln\left(\frac{mass_{235}}{mass_{238}}\right)}$$

$$MBCR^{23X/23Y} = Avg\ R^{23X/23Y}_{meas} \cdot \left(\frac{mass\ 23X}{mass\ 23Y}\right)^{\beta}$$

Ion Counter Gain Corrections

$$GF^{23X/238} = \frac{R^{23x/238}_{True}}{R^{23x/238}_{M.B.\ Corr\ set\ x}}$$

QC Gain Corrected Ratio

$$R^{23X/238}_{corr} = MBCR^{23X/238} \cdot GF^{23X/238}$$

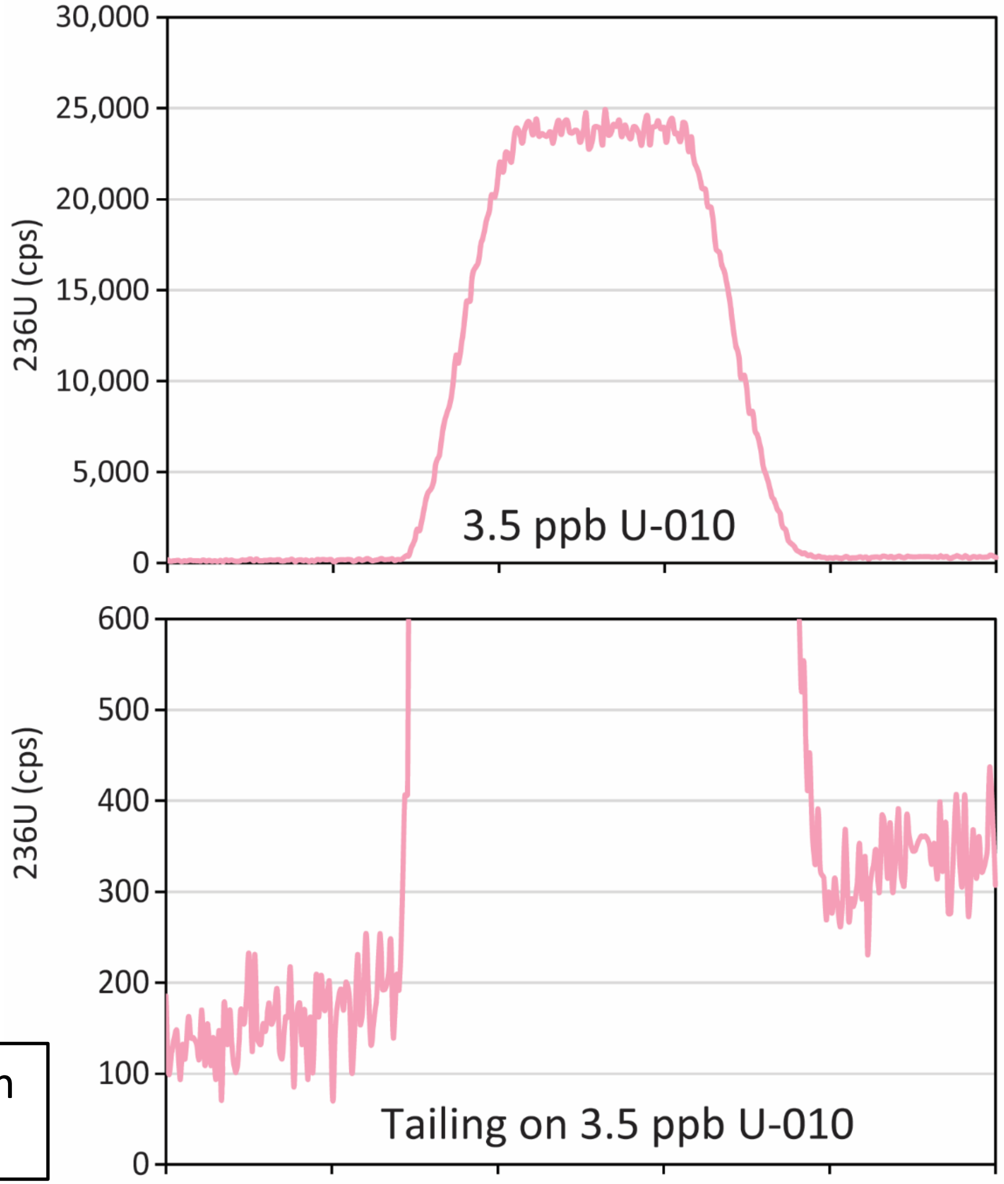
Pa Sample Gain Corrected Ratio

$$R^{231/233}_{corr} = MBCR^{231/233} \cdot \left(\frac{GF^{234/238}}{GF^{236/238}}\right)$$

Traced Pa: Abundance Sensitivity

Traced Pa Bracketing Standard U Isotope Compositions						
CRM	$^{234}U/^{238}U$	Unc. (k=2)	$^{235}U/^{238}U$	Unc. (k=2)	$^{236}U/^{238}U$	Unc. (k=2)
U010	5.45×10^{-5}	0.14%	0.010138	0.10%	6.92×10^{-5}	0.083%
U005-A	3.42×10^{-5}	0.14%	0.005092	0.10%	1.20×10^{-5}	0.083%

- U010, U005-A: well-constrained uncertainties
- > 98% ^{238}U abundance in standards
  - Tailing from ^{238}U effects $^{236}U/^{238}U$ and $^{234}U/^{238}U$ ratios
  - Impact ion counter gain calculations calculated from U010 and applied to U005-A QCs and Pa samples



~250 cps tail from ^{238}U on ~25,000 cps ^{236}U peak

Traced Pa: Abundance Sensitivity

- Baselines measured prior to each U standard (U010) and QC (U005-A) in the run
  - Capture any changes in tail magnitude that may result from plasma fluctuations during run
- Four baseline points measured to calculate exponential curve
  - 0.5 AMU above and below center mass
  - 0.35 AMU above and below center mass

Cup Configuration: pa_ic.ccf

Number of Blocks: 1 — Cycles/Block: 7

Measure first line every 1 cycles

Line No.	Mass Set	IC5	RPQ/IC3 A	IC2 L5	IC2 L5	RPQ/IC1 B	L4	L3	RPQ/IC1 C	Integration Time[s]	Number of Integrations	Idle Time [s]	Control Cup Peakcenter	Control Cup Focus	Jump Mode
1	05amu_Down	233U	234U	235U	235U	236U	238U		254.01	0.131	5	1.000	NONE	NONE	
2	035amu_Down	233U	234U	235U	235U	236U	238U		254.16	0.131	5	1.000	NONE	NONE	Normal
3	035amu_Up	233U	234U	235U	235U	236U	238U		254.86	0.131	5	1.000	NONE	NONE	Normal
4	05amu_Up	233U	234U	235U	235U	236U	238U		255.01	0.131	5	1.000	NONE	NONE	Normal

U Baseline Method

Run prior to each U010 and U005-A in the run

Cup Configuration: pa_ic.ccf

Number of Blocks: 1 — Cycles/Block: 40

Line No.	Mass Set	IC5	RPQ/IC3 A	IC2 L5	IC2 L5	RPQ/IC1 B	L4	L3	RPQ/IC1 C	Integration Time[s]	Number of Integrations	Idle Time [s]	Control Cup Peakcenter	Control Cup Focus	Jump Mode
1	Main	233U	234U	235U	235U	236U	238U	242.692	254.51	4.194	1	3.000	NONE	NONE	

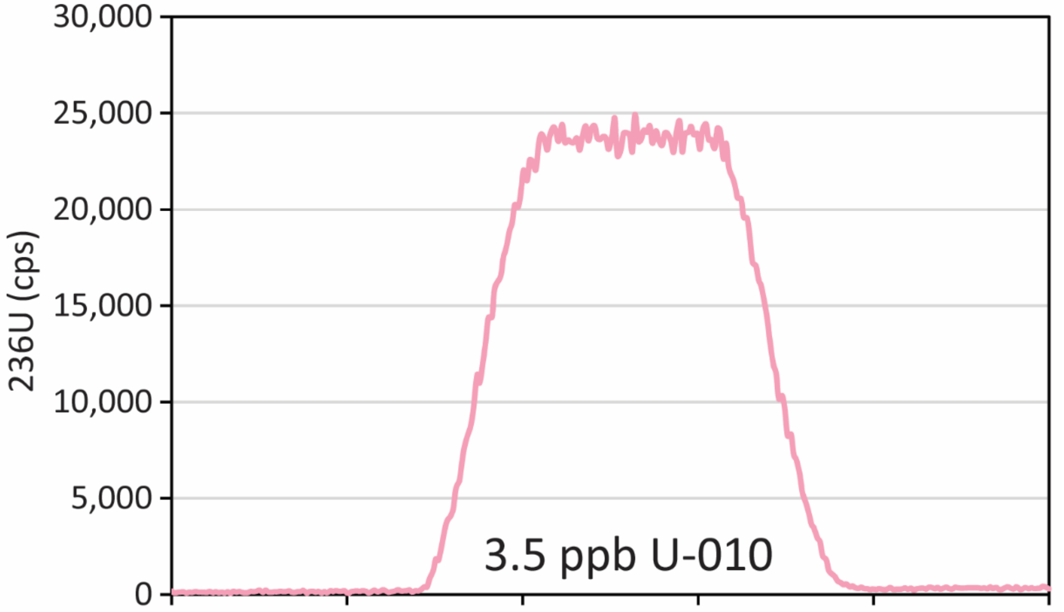
U Method

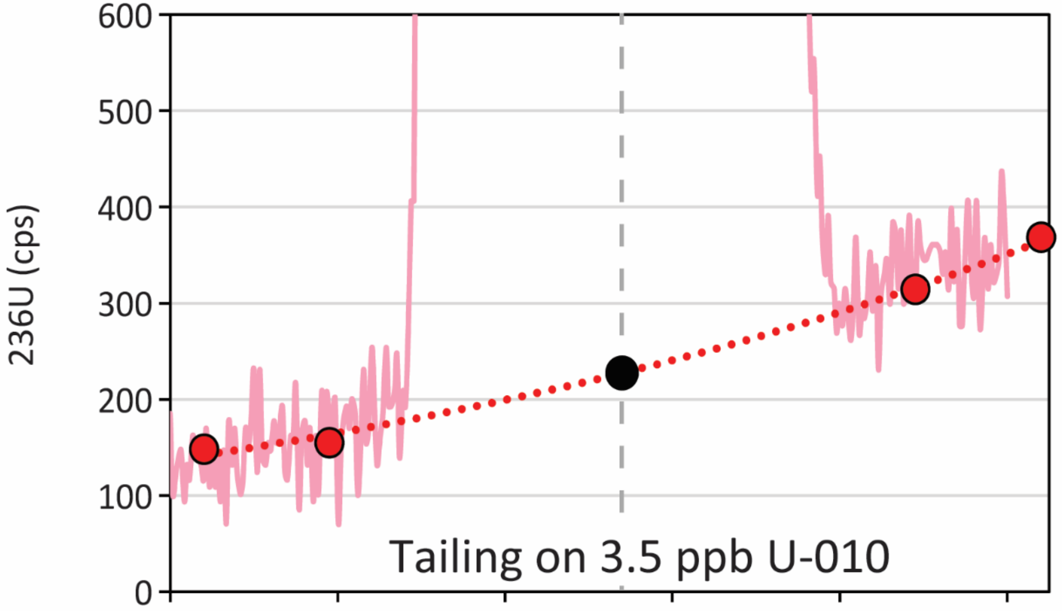
Run for each U010 and U005-A in the run

Traced Pa: Abundance Sensitivity

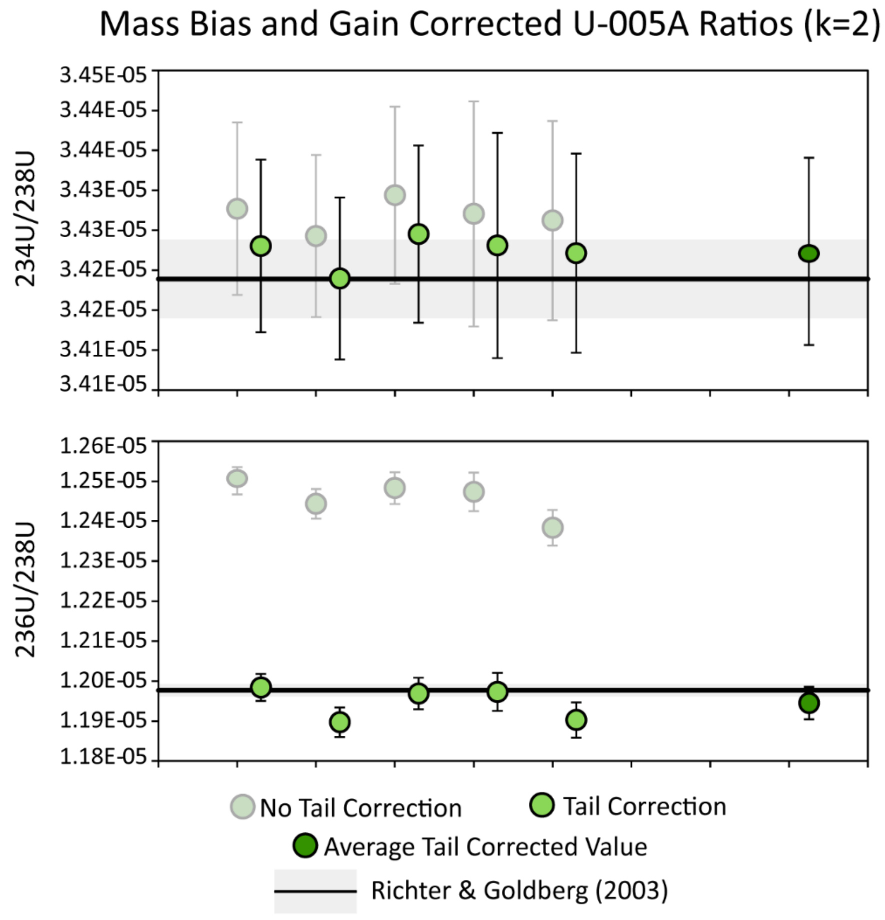
U010 ^{236}U Baseline Measurements and Tail Calculations					
Cycle	**0.50 amu below CM (cps)**	**0.35 amu below CM (cps)**	**0.35 amu above CM (cps)**	**0.50 amu above CM (cps)**	**Calculated 236 Tail at CM (cps)**
1	146.49	144.97	279.25	354.02	214.05
2	143.44	155.65	305.19	375.38	224.89
3	138.86	144.97	294.51	364.70	215.64
4	157.17	155.65	321.97	367.75	231.99
5	163.28	163.28	326.55	367.75	237.87
6	166.33	172.43	352.49	367.75	246.93
7	123.61	149.55	323.50	384.53	218.98
Average:					**227.19**
STDEV:					**12.28**

- Counts at four off-peak masses input into Excel growth function to calculate and subtract tailing



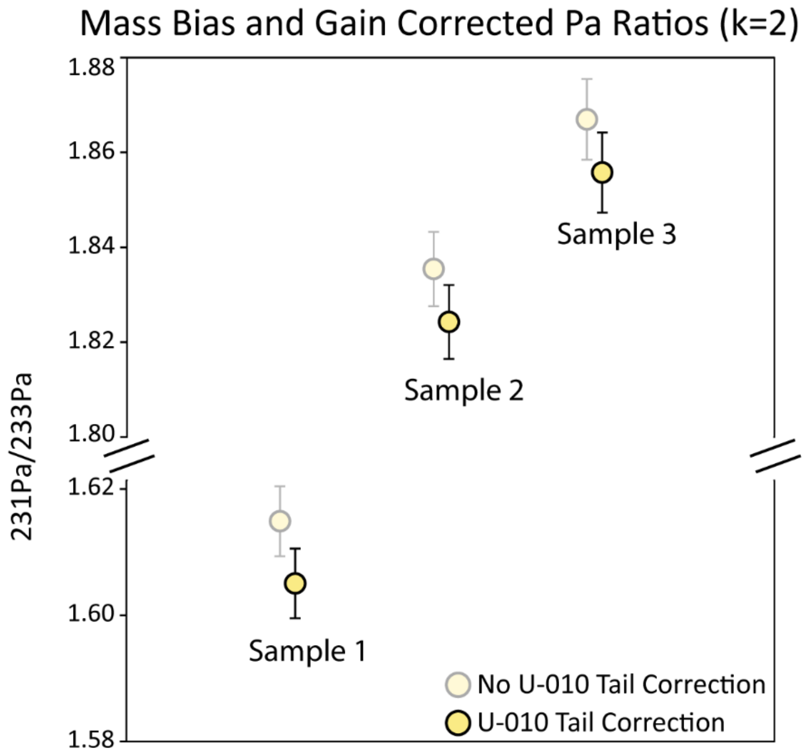


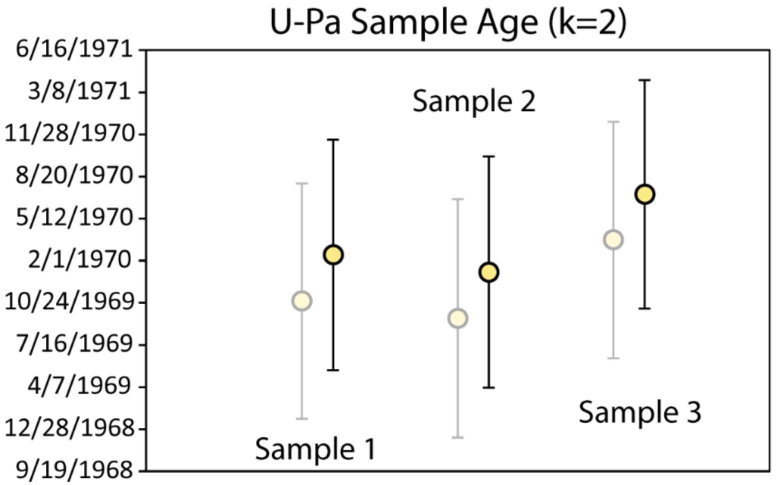
Traced Pa: Tail Correction Assessment



- **U005-A** $^{234}U/^{238}U$ and $^{236}U/^{238}U$ ratios demonstrate importance of tail corrections on minor isotopes in U010 and U005-A

- No tail corrections made to ^{231}Pa and ^{233}Pa isotopes
- **PaT samples** less sensitive to tail corrections made in mass bias and gain standard (U010)
- Without Pa standard, tail corrections vital to ensuring validity of instrumental bias corrections





Untraced U: Instrument Setup

Untraced U Sequence

- U Standard 1
- Wash 1
- Wash 2
- Acid Blank
- U Standard 2
- Wash 1
- Wash 2
- Acid Blank
- UxI Sample 1
- Wash 1
- Wash 2
- Acid Blank
- UxI Sample 2
- Wash 1
- Wash 2
- Acid Blank
- U Standard 1
- Wash 1
- Wash 2
- Acid Blank
- U Standard 2
- ⋮

Untraced U Neptune Plus Cup Configuration						
	IC5	**IC3**	**IC2**	**L5**	**IC1 B**	**L4**
U Samples/QCs	^{233}U	^{234}U	^{235}U	^{235}U	^{236}U	^{238}U
U Standards	^{233}U	^{234}U	^{235}U		^{236}U	^{238}U

Ion Counter

Faraday

Untraced U Sample
^{235}U on Faraday or ion counter

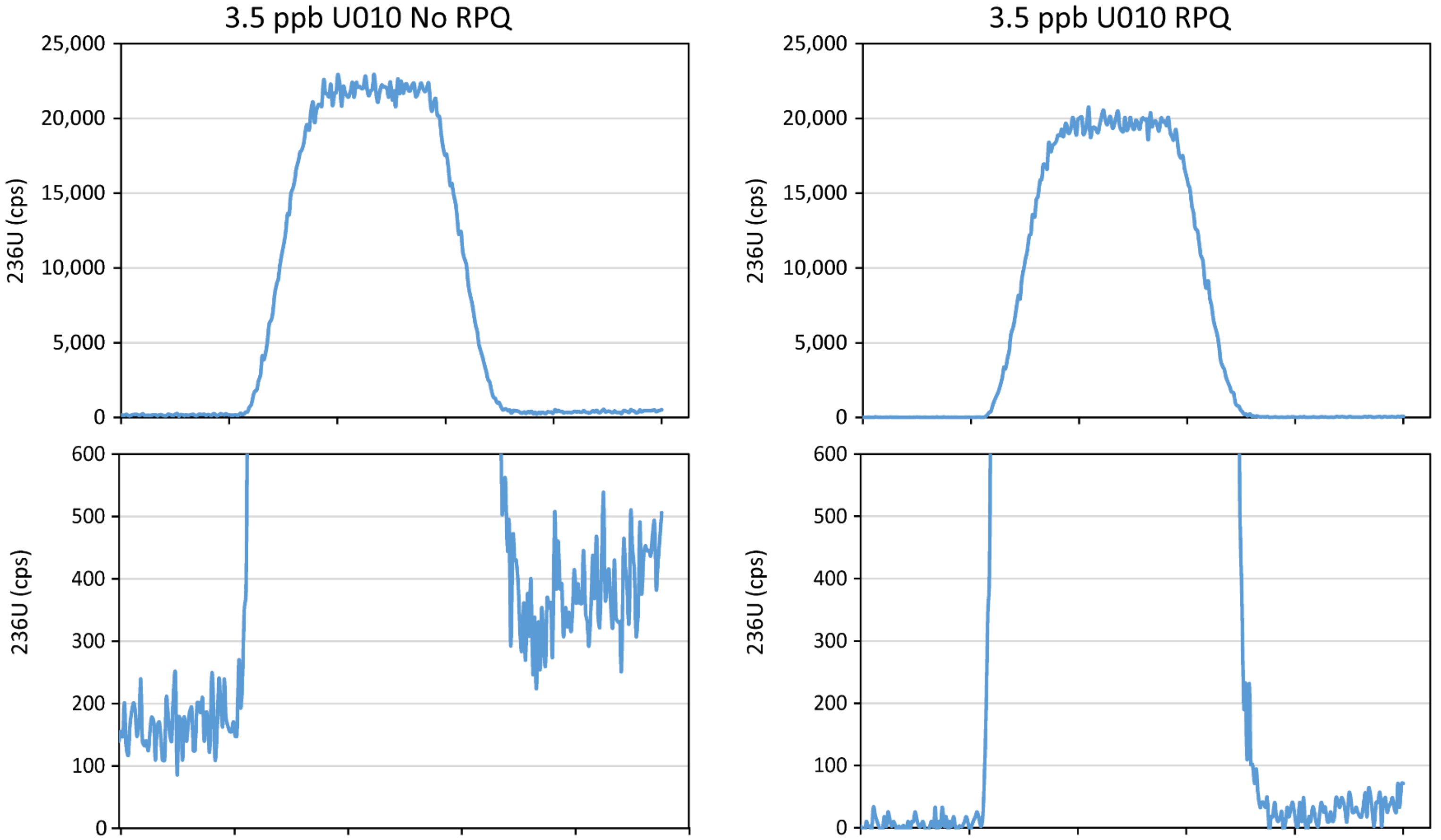
U standard 1
(e.g. U010, U050, U500, U850)
Mass Bias and Gain Corrections

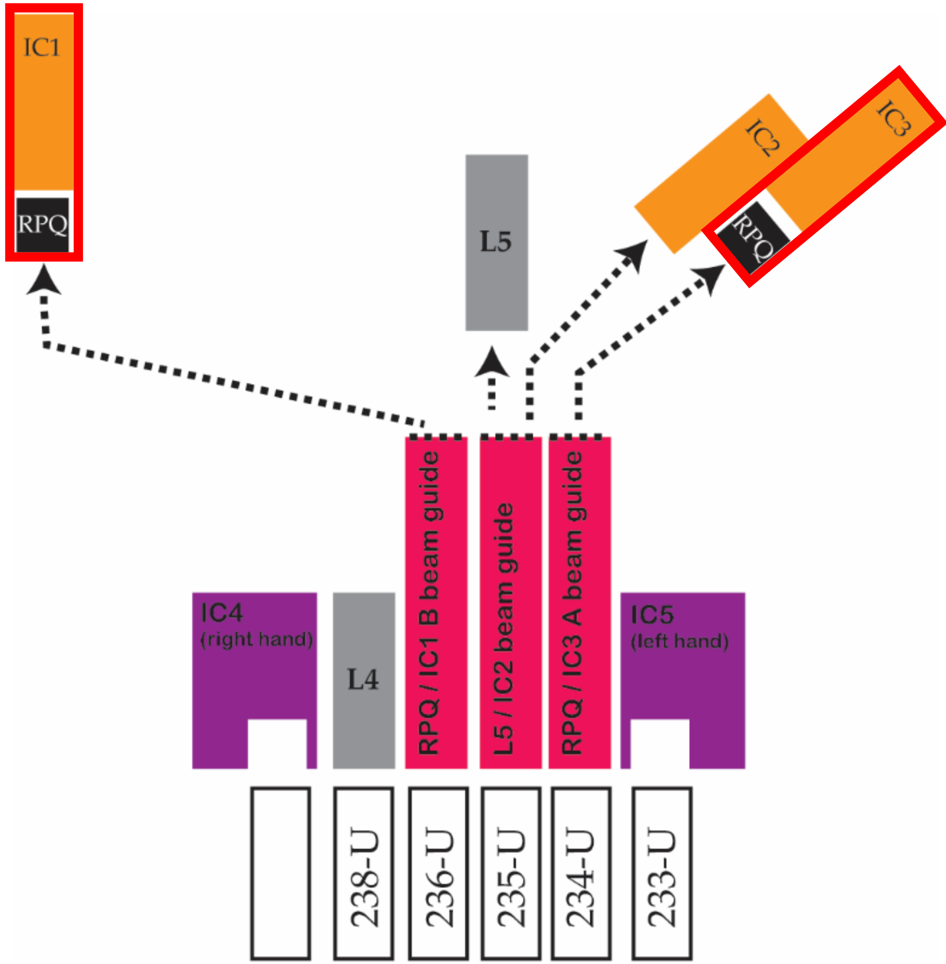
U QC Standard
(e.g. U005-A, U960, U010)
U composition similar to samples

- U samples screened prior to analysis
  - Standards with similar U isotopic compositions are selected to bracket samples
- Mass bias and gain corrections as in PaT method
  - Additional bracketing standard added to sequence if ^{235}U run on ion counter in sample/QC to correct for IC2 gain

Untraced U: Abundance Sensitivity

- Tailing on ^{236}U or ^{234}U managed by RPQs (energy filters)
  - No RPQs in PaT method- U in standard and Pa in samples may have different transmissions through RPQs
- No RPQ on IC5: tailing on ^{233}U corrected by 4 point baseline method (when needed)





Traced U: Instrument Setup

Traced U Sequence

- U Standard 1
- Wash 1
- Wash 2
- Acid Blank
- U Standard 2
- Wash 1
- Wash 2
- Acid Blank
- UxT Sample 1
- Wash 1
- Wash 2
- Acid Blank
- UxT Sample 2
- Wash 1
- Wash 2
- Acid Blank
- U Standard 1
- Wash 1
- Wash 2
- Acid Blank
- U Standard 2
- ⋮

U standard 1
(e.g. IRMM 74-1, U500)
Mass Bias Corrections

U QC Standard
(e.g IRMM 74-2)
U composition similar to samples

Traced U Neptune Plus Cup Configuration					
	L2	**L1**	**C**	**H1**	**H2**
U Samples/QCs	233U	234U	235U	236U	238U
U Standards	233U	234U	235U	236U	238U

Ion Counter

Faraday

- UxT samples typically traced with 1:1 ratio of ^{233}U:^{238}U or ^{233}U:^{235}U
- All U isotopes measured on Faradays
- Typically include standards with ^{233}U as bracketing standard and/or QC
- Exponential mass bias corrections applied using $^{233}U/^{238}U$ or $^{233}U/^{235}U$ ratio of bracketing standard

^{235}U-^{231}Pa Chronometry Sample Analysis: Summary

- **PaT and UxI measurements**: combination of ion counters and Faradays
  - Mass bias corrections made with $^{235}U/^{238}U$ ratios (Faraday-Faraday)
  - Gain corrections made using minor U isotope ratios (ion counter-Faraday)
  - Abundance sensitivity improved using baseline measurements (PaT) or RPQs (UxI)

- **UxT measurements**: Faraday measurements
  - Mass bias corrections with $^{233}U/^{238}U$ or $^{233}U/^{235}U$ (Faraday-Faraday) ratios